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## ELUCIDATION OF REACTION MECHANISMS FOR THERMAL ELIMINATIONS AND RING CLOSURES BY PYROLYSIS-GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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## SUMMARY

A pyrolysis-gas chromatographic-mass spectrometric analysis system has been used to study the course of certain thermolytic reactions involving eliminations and ring closures. Reaction conditions for the difficultly prepared isoindoles have been established and the products have been characterized in the gas phase by mass spectrometry. A possible synthetic route to benzofurazans and related heterocycles has been indicated by studies of thermally induced ring closure reactions.

## INTRODUCTION

Pyrolysis techniques have provided not only the basis for a wide variety of analytical procedures<sup>1-3</sup>, but also the means for elucidating the behavior of compounds involved in various thermal processes<sup>4-6</sup>. The technique has been shown to be very useful for studies of thermal and/or catalytic conversions on a micro-scale<sup>7</sup>. In the present study a pyrolysis-gas chromatographic-mass spectrometric (GC-MS) analysis system has been used to study certain thermal reactions involving eliminations and ring closures.

The method has been found to have particular efficacy for elucidating the course of reactions which occur in the vapor state, but in which the products cannot readily be isolated in the condensed phase.

Two systems have been studied as examples of the technique: (1) formation of isoindoles by thermal elimination and (2) formation of benzofurazans by ring closure.

## EXPERIMENTAL

Fig. 1 shows a schematic diagram of the combined pyrolysis-GC-MS analysis system. The system is designed to provide the means for carrying out a wide variety of pyrolysis studies using various types of pyrolyzers and under varying conditions of time, temperature, atmospheric environment, and physical state of the sample. The

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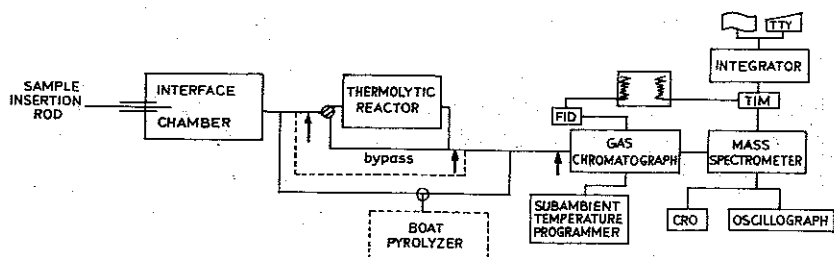


Fig. 1. Schematic diagram of the analysis system. CRO = Cathoda ray oscilloscope; FID = flame ionization detector; TIM = total ion current monitor; TTY = teletype.

pyrolysis products are separated by the gas chromatograph and the individual components identified by mass spectrometry. The configuration employed in these studies utilized the following components: A Chemical Data System Model 1100 Pyrochrom vapor phase pyrolysis unit (for the isoindole study), a Fisher/Victoreen Series 4400 boat pyrolyzer (for the benzofurazan study), a Bendix Model MA-2 time of flight mass spectrometer, and a Bendix Model 2200 gas chromatograph. The solids interface used to volatilize the epimino compounds for subsequent pyrolysis in the vapor phase reaction was a Chemical Data Systems Pyroprobe 100 Injection Interface Model CDS-100-374. A special insertion probe for introducing small samples (*ca.* 1  $\mu$ g) was constructed in the laboratory as shown in Fig. 2.

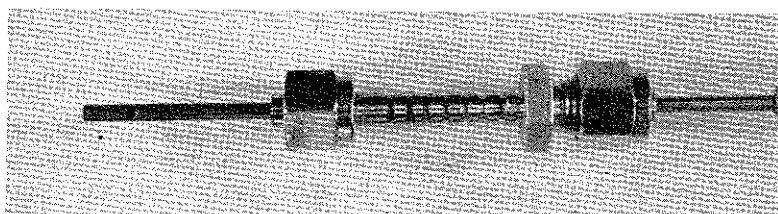


Fig. 2. Photograph of the sample insertion probe.

The chromatography column employed throughout was a 6 ft.  $\times$  1/8 in. I.D. column packed with 10% SE-30 on 80–100 mesh Chromosorb. The flow-rate of helium carrier gas was usually about 20 ml/min. Since the mass spectrometer is equipped with a high-capacity vacuum system, 1/8-in. packed columns may be used without a separator at flow-rates up to 25 ml/min. The chromatographic column chamber is fitted with a subambient temperature programmer controller so that the pyrolysis products may be collected on the cold column to achieve efficient narrow band elution behavior as the components are subsequently eluted.

The time of flight mass spectrometer provides certain advantageous output features such as predynode gating circuitry at the election multiplier which permits unwanted contributions such as carrier gas, water, carbon dioxide or other gross diluents to be eliminated from the total ion current display which serves as the chromatographic record. In addition to the usual analog recording the output of the total ion current monitor of the mass spectrometer is fed to a digital integrator which provides a teletype printout of the GC data, or a paper tape output which can subsequently be processed by a computer. A variety of output presentations is also

available for the mass spectrum output. This is displayed on an oscilloscope, recorded on an oscillograph, or digitized on-line by means of a spectrum digitizer (Columbia Scientific Industries Model 260).

### Materials

The chemicals used in this study were normally of purified quality. Certain of the reference compounds were prepared and characterized in the laboratory. These were: 1,4-imino-1,2,3,4-tetrahydronaphthalene<sup>8</sup>, 1,4-imino-1,2,3,4-tetrahydroanthracene<sup>9</sup>, N-benzyl-1,4-imino-1,2,3,4-tetrahydroanthracene<sup>10</sup>, benzofurazan<sup>10</sup>, benzofurazan oxide<sup>10</sup>, 5-methylbenzofurazan<sup>10</sup>, and 5-methylbenzofurazan oxide<sup>10</sup>.

### Procedures

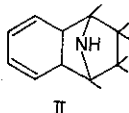
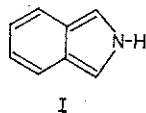
In the study of the thermal elimination reactions of the imino compounds, 10- $\mu$ g samples were placed in the hole of the insertion probe (Fig. 2) and after fitting the holder to the interface, the probe was moved into the heated area, which was held at 325°. The volatilized compounds were transferred to the vapor phase pyrolyzer by means of helium carrier gas. Continuously, after pyrolysis at the selected temperature, the products were swept onto the chromatography column.

In the study of the pyrolysis of nitroaniline and the nitrotoluidines about 50- $\mu$ g samples were placed in stainless-steel boats and the boats inserted in the furnace tube. The temperature was then raised to 800° in about 1 sec and the pyrolysis products swept onto the chromatography column with helium.

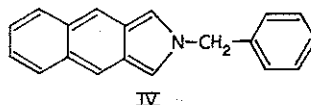
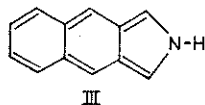
## RESULTS AND DISCUSSION

### Thermal elimination reactions

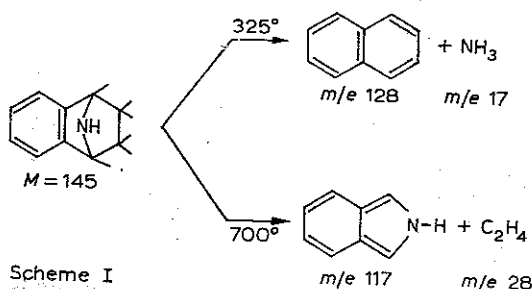
The unsubstituted isoindoles have been unknown until recently because of their propensity to polymerize. The synthesis of isoindole (I) by means of an elimination reaction (retro-cyclo-addition) has been reported<sup>8</sup>.



The compound appears to be formed readily at 600° by vacuum thermolysis of iminonaphthalene (II) in a quartz tube by elimination of ethylene, but characterization of the products involves isolation at liquid nitrogen temperature and derivatization in the cold (e.g. at dry-ice temperature). The corresponding syntheses of homologs such as benzoisoindole (III) or N-benzylbenzoisoindole (IV) have met with only partial success because of the difficulties in isolation and characterization of the products. A good yield of III appears to be isolated in a liquid nitrogen cold trap. However, because of its high reactivity, spectral data for proof of structure could



be obtained only at low temperatures. By simulating the reactions in the micro pyrolysis unit and characterizing the products in the gas phase it is possible to elucidate the course of these elimination reactions.

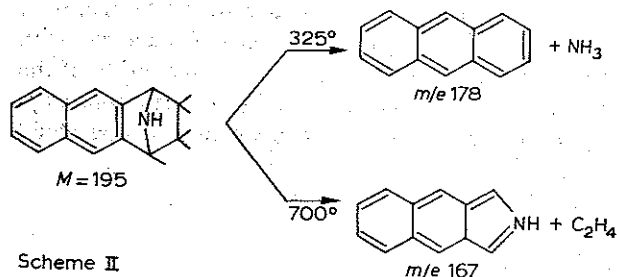


Thermal decomposition of the imino compound, *e.g.* 1,4-imino-1,2,3,4-tetrahydronaphthalene (II), may follow two routes as depicted in Scheme I. The course of these reactions is temperature dependent as seen in the chromatograms displayed in Fig. 3. Both reactions occur over the range of temperature studied, but the relative yields are changed markedly at the high and low temperatures. Although appreciable amounts of ethylene are seen evolved at 325°, no isoindole may be detected (as *m/e* 117 as the parent ion in the mass spectrum) in any of the spectra. A prominent GC peak having a mass spectrum with a parent ion at *m/e* 128 and a spectral pattern corresponding to naphthalene is seen in the chromatogram of the pyrolysis products obtained at 325°. Correspondingly, a spectrum corresponding to  $\text{NH}_3$  is observed in the spectrum scans although no GC peak is seen on the total ion monitor (masses 4–20 are gated out by the predynode gating circuit).

At 700°, the formation of the isoindole in good yield is clearly indicated by the large GC peak having a mass spectrum which corresponds to that reported for the isolated compound by Bornstein *et al.*<sup>8</sup> and by Bonnett and Brown<sup>11</sup>.

Small amounts of naphthalene are formed (no  $\text{NH}_3$  is detected) and some toluene is observed. The large amount of ethylene seen at 325° without a corresponding amount of the isoindole cannot be readily explained. If isoindole is formed, the temperature seems too great to permit condensation, and the dilution in the carrier gas seems to preclude intermolecular reaction. Other reactions may be occurring, but no evidence from the GC or MS data can be adduced.

The formation of benzoisoindole from iminoanthracene, *i.e.* 1,4-imino-1,2,3,4-tetrahydroanthracene, has been studied in somewhat greater detail. The reaction follows the same course as that of iminonaphthalene, as seen in Scheme II.



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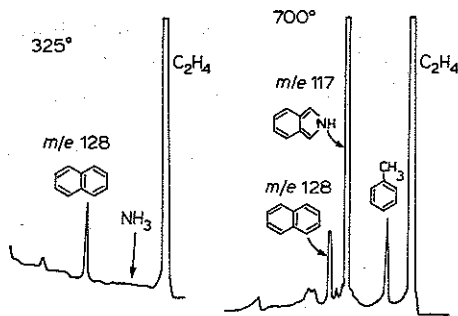


Fig. 3. Chromatograms of pyrolysis products of iminonaphthalene.

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Programmed-temperature chromatograms of the pyrolysis products obtained at various temperatures are seen in Fig. 4. The main product with the vapor phase reactor at 325° is anthracene. As in Fig. 3, ammonia is detected by the mass spectra, but not seen on the total ion current output record shown here. At 500° anthracene is also the main product but a trace of benzoisindole may be detected. At 675°, more benzoisindole than anthracene is produced and at 800° the main product is benzoisindole. The relative yield of benzoisindole as a function of temperature is depicted in the graph shown in Fig. 5.

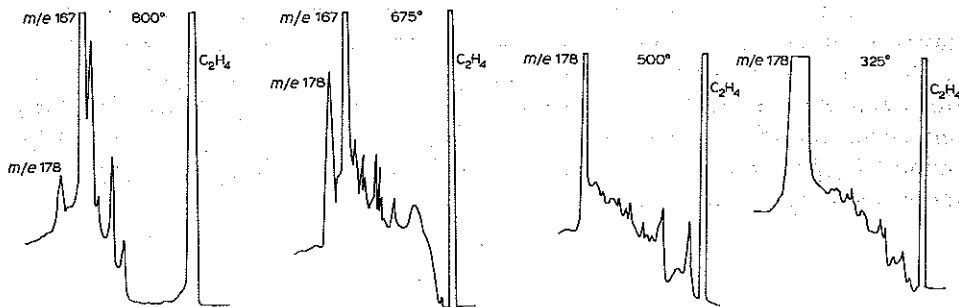


Fig. 4. Chromatograms of pyrolysis products of epiminoanthracene at various temperatures.

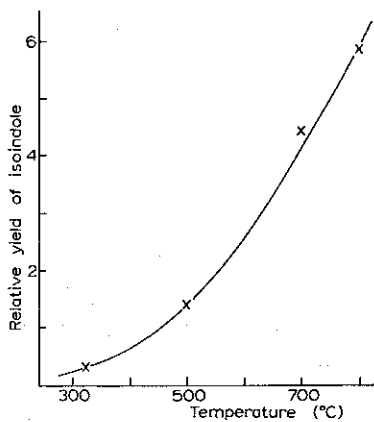
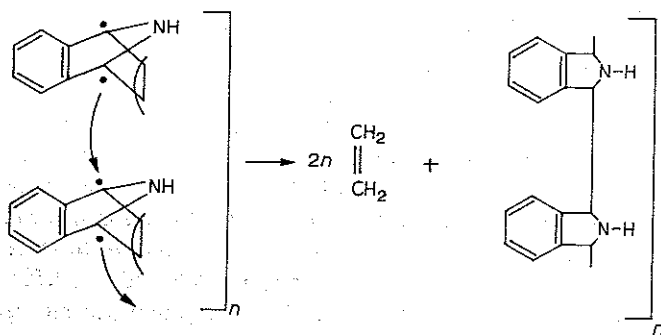


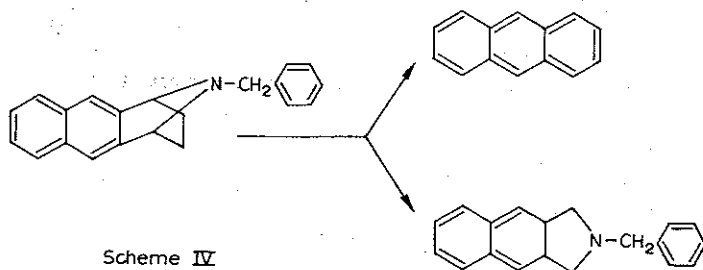
Fig. 5. Graph of yield of benzoisindole as a function of temperature.

Large amounts of ethylene are seen in all the chromatograms even at the lower temperature where no benzoisindole is seen. It appears that some additional reaction producing ethylene is occurring. Since a residue is observed on the solids insertion probe, it may be postulated that an intermolecular reaction yielding a polymeric and therefore non-volatile compound, may be taking place in the interface chamber depicted in Scheme III.



Scheme III

Attempts to prepare N-substituted benzoisindoles by an elimination reaction have been unsuccessful on a preparative scale. In order to evaluate this reaction, it also was studied by micro-simulation with the pyrolysis-GC-MS analysis system. The reactions were expected to be analogous to those of the iminonaphthalene (Scheme I) and iminoanthracene (Scheme II). The starting compound was N-benzyl-1,4-imino-1,2,3,4-tetrahydroanthracene and was expected to yield N-benzylbenzoisindole (according to Scheme IV).



Scheme IV

As seen in the chromatograms shown in Fig. 6, the N-benzyl derivative is not observed. The products are essentially those obtained for iminoanthracene itself except for the presence, in addition, of toluene and benzonitrile. As expected, the benzoisindole is detected at the higher temperature and anthracene at the lower, but the amount of each is very small. Toluene and benzonitrile are the main products, indicating cleavage of the benzylamine and at low temperature (*i.e.*, 325°) iminoanthracene itself is found. A product having a parent ion of 181 is observed, but identification of this compound is not yet confirmed.

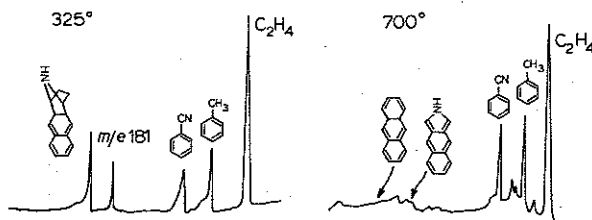


Fig. 6. Chromatograms of pyrolysis products of N-benzyliminoanthracene.

The information concerning the course of these reactions has been invaluable to the chemists concerned with preparation of these compounds.

#### Ring closures

Pyrolysis reactions may be used very effectively as the basis for qualitative identification<sup>12-14</sup> of various substances. When in a recent study of a pyrolytic method for the identification of nitrotoluidine isomers<sup>15</sup> it became apparent that heterocyclic ring compounds were being formed, the possibility of a new synthetic route was suggested.

Chromatograms of the pyrolysis products formed from *o*- and *p*-(*m*-nitro)-toluidine are shown in Fig. 7. The major component in each case has been shown by mass spectrometry to be a compound having a mass of 134. The compound derived by pyrolysis from the nitro-*o*-toluidine (I) has been characterized as 5-methylbenzofurazan (II) according to Scheme V. 5-Methylbenzofurazan oxide (5-methylbenzofuroxan) (III) was prepared through a series of reactions from the nitrotoluidine (I) which subsequently upon pyrolysis or reduction with triphenylphosphine gave IV and V. Mass spectra of compounds III, IV and V, as seen in Fig. 8, were found to be identical.

Benzofurazan may be synthesized from *o*-nitroaniline in a similar manner as shown in Scheme VI.

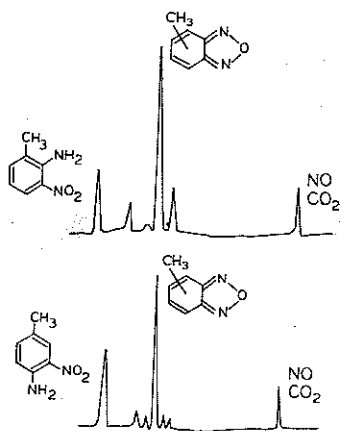
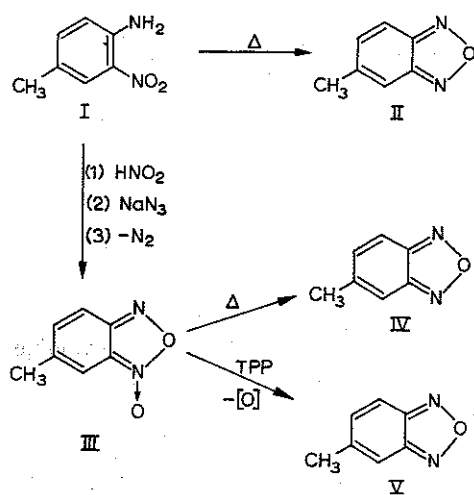


Fig. 7. Chromatograms of pyrolysis products from *o*- and *p*-(*m*-nitro)-toluidines.



Scheme V

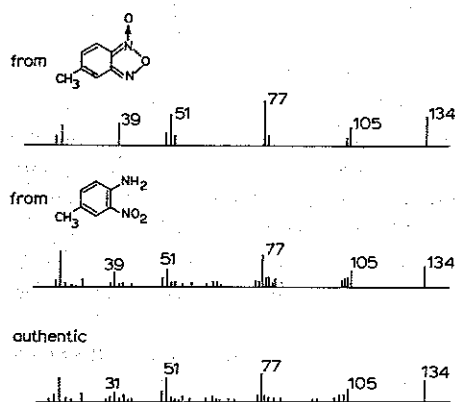
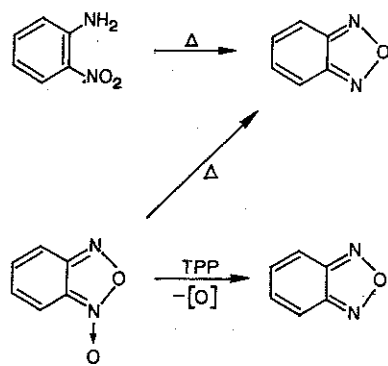


Fig. 8. Comparison of mass spectra of certain pyrolysis products and authentic 5-methylbenzofurazan.



Scheme VI



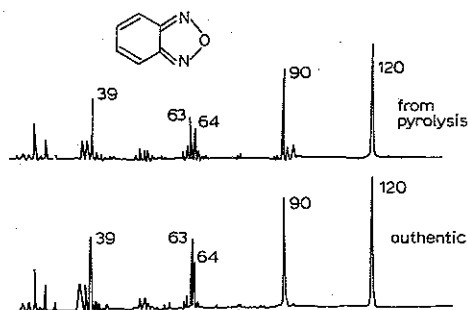


Fig. 9. Comparison of mass spectra of the pyrolysis product of nitroaniline and authentic benzofurazan.

Again, as seen in Fig. 9, the mass spectra of the pyrolysis product and the synthesized authentic compound are identical. A pyrolysis method of preparation for the benzofurazans may prove to provide a better synthetic route than the current methods, which involve several steps.

#### REFERENCES

- 1 R. L. Levy, *Chromatogr. Rev.*, 8 (1967) 49.
- 2 D. A. Leathard and B. C. Shurlock, *Identification Techniques in Gas Chromatography*, John Wiley, London, 1970, p. 123.
- 3 S. G. Perry, *Advan. Chromatogr.*, 7 (1968) 221.
- 4 W. Simon, P. Kriemier, J. A. Voellmin and N. Steiner, *J. Gas Chromatogr.*, 7 (1967) 53.
- 5 M. Gassiot-Matas and E. Julia-Danes, *Chromatographia*, 5 (1972) 493.
- 6 N. Kwart, S. F. Sarner and J. H. Olson, *J. Phys. Chem.*, 73 (1969) 4056.
- 7 G. Schomburg, R. Rienacker and R. G. Schaefer, *Chromatographia*, 5 (1972) 532.
- 8 J. Bornstein, D. E. Remy and J. E. Shields, *J. Chem. Soc., Chem. Commun.*, (1972) 1149.
- 9 J. Bornstein and D. E. Remy, in preparation.
- 10 J. H. Cornell, in preparation.
- 11 R. Bonnett and R. F. C. Brown, *J. Chem. Soc., Chem. Commun.*, (1972) 393.
- 12 C. Merritt, Jr., C. DiPietro and M. L. Bazinet, *Proceedings of the Nineteenth Annual Conference on Mass Spectrometry and Allied Topics*, American Society for Mass Spectrometry, 1971, p. 224.
- 13 C. Merritt, Jr. and C. DiPietro, *Anal. Chem.*, 44 (1972) 57.
- 14 C. Merritt, Jr., C. DiPietro, D. H. Robertson and E. J. Levy, *J. Chromatogr. Sci.*, 12 (1974) 668.
- 15 C. Merritt, Jr., *Proceedings of the Twenty-third Annual Conference on Mass Spectrometry and Allied Topics*, American Society for Mass Spectrometry, 1975, in press.